

## Photoconductor for electrophotography

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### Abstract

A metal carboxylate of the following general Formula (I), (II), or (III), wherein Ar1 represents an optionally substituted arylene group, Ar2 represents one of the group consisting of an alkyl group, an optionally substituted aryl group, an aralkyl group, and a hydrogen atom, X represents a metal atom selected from the group consisting of tin, zinc, cobalt, nickel, iron, and chromium, and n represents the valence of X, is added to the charge transport layer of a photoconductor for electrophotography. The resulting photoconductor exhibits excellent electric stability in repetitive use with little variation in electrically charged potential or residual potential.

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## Description

### BACKGROUND OF THE INVENTION

The present invention relates to a photoconductor for electrophotography. More specifically, the present invention relates to a photoconductor for electrophotography useful in printers, copiers, and the like, having improved additives in an organic charge transport layer. Even more specifically, the present invention provides a photoconductor having a small variation in the charged potential between the initial charged potential and the charged potential after repeated use. The present invention further provides a photoconductor having a small variation in the residual potential between the initial residual potential and the residual potential after repeated use.

A photoconductor for electrophotography, hereinafter also referred to as simply a photoconductor, has a photoconductive layer formed on a conductive substrate. An organic photoconductor, which employs charge-generating or charge-transporting organic compounds for the photoconductive layer, has been researched and developed in recent years. The organic photoconductor has been applied to the fields of copying, printing, and the like, taking advantage of the variety, high productivity, and safety of the organic material.

The organic photoconductor has several functions in electrophotography. The organic photoconductor must maintain a surface charge in darkness, receive light and generate carriers, and transport the generated carriers. The organic photoconductor is classified in two categories, either a single-layered type, or a function-separated multi-layered type. The organic photoconductor of the single-layered type has a photoconductive layer performing all the above functions. The function-separated, multi-layered photoconductor has a photoconductive layer consisting of a charge generation layer and a charge transport layer. The charge generation layer generates charges on exposure to light. The charge transport layer

preserves surface charges in darkness. Additionally, the charge transport layer transports the charges generated in the charge generation layer on exposure to light.

Recently, the function-separated, multi-layered organic photoconductor has been chiefly used in the field of electrophotography. The photoconductive layer of the function-separated and multi-layered organic photoconductor consists of a charge generation layer and a charge transport layer. Applying a coating liquid to a conductive substrate forms the charge generation layer. The coating liquid for the charge generation layer is prepared by dispersing charge-generating organic pigment and a resin binder in an organic solvent. Applying a second coating liquid forms the charge transport layer. The coating liquid for the charge transport layer is prepared by dissolving charge-transporting low molecular weight organic compound and a resin binder in an organic solvent.

The properties of a conventional organic photoconductor, however, do not necessarily satisfy all the specified demands. Some of the above stated properties have a strong opportunity for improvement. For example, the property of electric stability in repetitive use has significant room for improvement over the current technology. The repeated and continuous use of a conventional photoconductor in an actual machine causes a variation in electrically charged potential or residual potential, resulting in a deteriorated printing quality.

A factor contributing to this potential variation is accumulation of the generated carriers in the organic photoconductive layer upon light exposure or charge erasing. More specifically, it is believed that the accumulation of the generated carriers originates from the trapping of carriers in the charge generation layer, in the charge transport layer, or at the interface of the two. Another factor is deterioration of the organic material, attributable to radiation, heat, and ozone generated during repetitive use of the photoconductor in an actual machine. Other environmental factors, such as changes in temperature or humidity contribute to the deterioration of the organic material of the photoconductor. Charge-generating materials and charge transporting materials have been recently positively improved. However, neither the means nor the materials have been found by which this problem can be adequately solved.

Moreover, the incorporation of conventional additives to the charge transport layer does not increase the stability of electrically charged potential and residual potential when the photoconductor is used repeatedly. The incorporation of some of the additives to the charge transport layer actually causes a negative effect, decreasing charged potential or increasing residual potential.

## OBJECTS AND SUMMARY OF THE INVENTION

It is an object of the present invention to provide an organic photoconductor which overcomes the foregoing problems.

It is another object of the present invention to provide an organic photoconductor having small variation in electrically charged potential and residual potential after repeated use.

It is a further object of the present invention to provide an organic photoconductor having excellent image characteristics.

A thorough research of additives has shown that the incorporation of a specific metal carboxylate to the charge transport layer is very effective for attaining the objects of the present invention. Incorporation of a specific metal carboxylate keeps a charged potential and a residual potential unchanged after repetitive use, without degrading other electric performances. The invention is effective in various combinations of charge generation layers and charge transport layers.

A first photoconductor of the present invention comprises a conductive substrate, an under-coating layer, and a photoconductive layer laminated successively on the conductive substrate. The photoconductive layer consists of the charge generation layer and the charge transport layer. The charge transport layer is formed on the charge generation layer. In addition, the charge transport layer contains a metal carboxylate represented by the following general formula (I), wherein Ar<sub>1</sub> represents an optionally substituted arylene group, X represents a metal atom selected from the group consisting of tin, zinc, cobalt, nickel, iron, and chromium, and n represents the valence of metal atom X.

A second photoconductor of the present invention comprises a charge transport layer containing a metal

carboxylate represented by the following general formula (II), wherein Ar1, n, and X represent the same functionality as previously described. The carboxylate ligand carries a skeleton stilbenyl group, in place of the metal carboxylate represented by the general formula (I) in the previously described first photoconductor.

A third photoconductor comprises a charge transport layer containing a metal carboxylate represented by the following general formula (III), wherein Ar1, n, and X represent the same functionality as those referred to in the first photoconductor, Ar2 represents an alkyl group, an optionally substituted aryl group, an arylalkyl group, or a hydrogen atom. The carboxylate ligand carries a skeleton hydrazonyl group, in place of the metal carboxylate represented by the general formula (I) of the previously described first photoconductor.

Briefly stated, the present invention provides a metal carboxylate of the following general Formula (I), (II), or (III), wherein Ar1 represents an optionally substituted arylene group, Arr2 represents one of the group consisting of an alkyl group, an optionally substituted aryl group, an aralkyl group, and a hydrogen atom, X represents a metal atom selected from the group consisting of tin, zinc, cobalt, nickel, iron, and chromium, and n represents the valence of X, being added to the charge transport layer of a photoconductor for electrophotography. The resulting photoconductor exhibits excellent electric stability in repetitive use with little variation in electrically charged potential or residual potential.

The above, and other objects, features and advantages of the present invention will become apparent from the following description read in conjunction with the accompanying drawing, in which like reference numerals designate the same elements.

#### BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic cross section of a function-separated, multi-layered type photoconductor.

#### DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1, a schematic cross section of a preferred embodiment of the photoconductor of the invention is depicted. The photoconductor is preferably a negatively charged, function-separated, multi-layered type photoconductor. The photoconductor includes an under-coating layer 2 coated on a conductive substrate 1. A photoconductive layer 3, on the under-coating layer 2, includes a charge generation layer 4 and a charge transport layer 5 successively formed thereon.

Conductive substrate 1 is both one of the electrodes of the photoconductor, and a supporting body for each of the layers that compose the photoconductor. Conductive substrate 1 is preferably a cylinder, a plate, or a film. The preferred materials of conductive substrate 1 include glass and resin that are surface-treated with conductive materials, and metals, such as aluminum, stainless steel, and nickel.

Under-coating layer 2, consisting of a metal oxide film, such as anodized aluminum, or a resinous layer, is formed if required. Under-coating layer 2 controls the injection of charge from conductive substrate 1 to photoconductive layer 3. Moreover, under-coating layer 2 coats any defects on the surface of conductive substance 1, while improving adhesiveness of photoconductive layer 3 to conductive substrate 2.

The resin used for under-coating layer 2 includes an insulating polymer, such as casein, polyvinyl alcohol, polyamide, melamine, and cellulose, and a conductive polymer, such as polythiophene, polypyrrole, and polyaniline. A plurality of these resins may be used for under-coating layer 2. Moreover, these resins may contain a metal oxide, such as titanium dioxide and zinc oxide.

Vacuum-depositing an organic photoconductive material as a charge generating material is a preferred method to form charge generation layer 4. Alternatively, charge generation layer 4 is formed by applying a coating liquid dispersed with particles of an organic photoconductive material and a dissolved resin binder.

Irradiating charge generation layer 4 generates carriers. It is necessary that the generation and the injection of carriers to charge transport layer 5 are efficient. The injection of carriers is preferably conducted with a small dependence on electric field. It is preferable that the injection of carriers to charge transport layer 5 is accomplished even with a minimal electric field.

Charge-generating materials include phthalocyanine compounds, such as metal-free phthalocyanine and titanylphthalocyanine. Another class of charge-generating materials include azo compounds, including bisazo compounds. Further charge-generating materials include pigments and dyes, such as quinone, indigo, cyanin, squarylium, azulonium, and pyrylium compounds.

The resin binder includes polyester resin, polyvinyl acetate resin, polyacrylate resin, polymethacrylate resin, polycarbonate resin, polyvinyl-acetoacetal resin, polyvinyl-propional resin, polyvinyl-butylal resin, phenoxy resin, epoxy resin, polyurethane resin, cellulose ester resin, and cellulose ether resin. A combination of the above resin can also be employed to create a suitable resin binder.

Five to 500 parts by weight of charge-generating material is used with respect to ten parts by weight of resin binder. The preferable range of the charge-generating material is from 10 to 100 parts by weight with respect to ten parts by weight of resin binder. The thickness of charge generation layer 4 is generally equal to or less than 5  $\mu\text{m}$ , preferably less than 1  $\mu\text{m}$ .

Charge transport layer 5 includes a charge-transporting material, a resin binder, and a metal carboxylate represented by the following general formula (I), (II) or (III), wherein Ar1 represents an optionally substituted arylene group, X represents a metal atom selected from the group consisting of tin, zinc, cobalt, nickel, iron, and chromium, n represents the valence of metal atom X, Ar2 represents an optionally substituted alkyl group, an optionally substituted aryl group, an optionally substituted arylalkyl group, or a hydrogen atom.

Preferred Ar1 groups include a phenylene group, a naphthylene group, and an anthrylene group, each of which may be substituted. Preferred substituents of Ar1 include an alkyl group, an aryl group, a hydroxy group, a halogen atom, an alkoxy group, an aryloxy group, an alkylcarbonyl group, an arylcarbonyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a carboxy group, and a cyano group.

Preferred Ar2 groups include a C1 -C3 alkyl group, and a phenyl group, each of which may be further substituted. Preferred substituents of the Ar2 group include a C1 -C3 alkyl group and a hydroxy group.

The following structures exemplify the embodiments of the metal carboxylate represented by the general formula (I), (II) or (III) where metal atom X is zinc. The metal atom X is not limited to zinc. Tin, cobalt, nickel, iron or chromium can also be used in place of zinc.

The metal carboxylate of the general formula (I) is exemplified in formulae (I-1) to (I-9). The metal carboxylate of the general formula (II) is exemplified in formulae (II-1) to (II-9). The metal carboxylate of the general formula (III) is exemplified in formulae (III-1) to (III-27).

The charge-transporting material preferably includes at least one of a hydrazone compound, a butadiene compound, a diamine compound, an indole compound, an indoline compound, a stilbene compound, and a distilbene compound.

The resin binder preferably includes at least one of a polycarbonate resin, such as a bisphenol A type, a bisphenol Z type, and a bisphenol A type-biphenyl copolymer, a polystyrene resin, and a polyphenylene resin.

Two to fifty parts by weight of the charge-transporting material is preferably used with respect to 100 parts by weight of the resin binder. A more preferable amount of the charge-transporting material is 3 to 30 parts by weight with respect to 100 parts by weight of the resin binder. The film thickness of charge transport layer 5 is in the range of 3  $\mu\text{m}$  to 50  $\mu\text{m}$  to preserve practically effective surface potential. Preferably, the film thickness of charge transport layer 5 is between 15  $\mu\text{m}$  to 40  $\mu\text{m}$ .

Preferably, 0.01 to 10 parts by weight of the metal carboxylate with respect to 100 parts by weight of the resin binder is incorporated into charge transport layer 5. More preferably, 0.1 to 3 parts by weight of the metal carboxylate with respect to 100 parts by weight of the resin binder is incorporated into charge transport layer 5.

In addition, an electron-accepting material, an antioxidant or a photostabilizer, may be incorporated into under-coating layer 2 and charge transport layer 5 to provide improved sensitivity, decreased residual potential, resistance to environment, and stability to harmful radiation. Such materials include a chroman

derivative, such as tocopherol, an ether, an ester, a polyarylethane compound, a hydroquinone derivative, a diether, benzophenone derivative, a benzotriazole derivative, a thioether, a phenylenediamine derivative, a phosphonate ester, a phosphite ester, a phenol, a hindered phenol, a straight-chain amine compound, a cyclic amine compound, and a hindered amine compound.

Additionally, a silicone oil or a fluorocarbon oil, is preferably incorporated into photoconductive layer 3 to facilitate flattening of the formed film by providing sufficient lubrication to the film surface.

Furthermore, a surface protective layer is optionally formed on photoconductive layer 3. The surface protective layer provides photoconductive layer 3 with resistance to environmental stresses as well as improved mechanical strength. The surface protective layer is composed of a material having resistance to mechanical and environmental stress. The material of the surface protective layer is chosen such that light, to which charge generation layer 4 is sensitive, penetrates with minimal loss in the surface protective layer.

## EXAMPLES

The following examples describe embodiments of the present invention.

### Example 1

An aluminum cylinder was used as a conductive substrate. A first coating liquid was dip-coated to the outer surface of the cylinder, and dried at a temperature of 100 DEG C. for 30 minutes. An under-coating layer of about 3 .mu.m thick was formed.

A first coating liquid was prepared as follows. Five parts by weight of alcohol soluble polyamide resin (CM8000 made by Toray Industries, Inc.) were dissolved in 90 parts by weight of methanol. Five parts by weight of titania corpuscles treated with aminosilane were dispersed in the methanol solution.

A second coating liquid was dip-coated on the under-coating layer and dried at a temperature of 80 DEG C. for 30 minutes. A charge generation layer of about 0.3 .mu.m thick was formed.

The second coating liquid was prepared as follows. One part by weight of phthalocyanine, as a charge generating material, was dispersed and 1.5 parts by weight of polyvinyl-butylal resin, as a resin binder, was dissolved in 60 parts by weight of dichloromethane. Phthalocyanine, represented by the following formula (A), coordinates with oxytitanium. The polyvinyl-butylal resin employed was "S-LEC KS-1" made by Sekisui Chemical Co., Ltd.

A third coating liquid was applied on the charge generation layer and dried for 60 minutes at a temperature of 90 DEG C., providing a charge transport layer having a thickness of 35 .mu.m. The third coating liquid was prepared by dissolving a charge-transporting material, and a zinc carboxylate in a solvent. The charge-transporting material was 90 parts by weight of the stilbene compound represented by the following Formula (B). The resin binder was 110 parts by weight of polycarbonate resin TOUGHZET B-500 made by Idemitsu Kosan Co. Ltd. The zinc carboxylate was 0.1 parts by weight of the carboxylate represented by the Formula (I-1). The solvent was 925 parts by weight of dichloromethane. Thus, the organic photoconductor of Example 1 was manufactured.

### Example 2

The photoconductor of Example 2 was prepared in the same way as that of Example 1 except that the zinc carboxylate of Formula (II-1) was used in place of that represented by Formula (I-1) in the Example 1. The zinc carboxylate of Formula (II-1) carries a skeleton stilbenyl group in the carboxylate ligand.

### Example 3

The photoconductor of Example 3 was prepared in the same way as that of Example 1 except that the zinc carboxylate of Formula (III-1) was used in place of that represented by Formula (I-1) in Example 1. The zinc carboxylate of Formula (III-1) carries a skeleton hydrazonyl group in the carboxylate ligand.

### Example 4

The photoconductor of Example 4 was prepared in the same way as that of Example 1 except that the zinc carboxylate of Formula (III-10) was used in place of that represented by Formula (I-1) in Example 1. The zinc carboxylate of Formula (III-10) carries a skeleton hydrazonyl group in the carboxylate ligand.

#### Example 5

The photoconductor of Example 5 was prepared in the same way as that of Example 1 except that the zinc carboxylate of Formula (III-19) was used in place of that represented by Formula (I-1) in Example 1. The zinc carboxylate of Formula (III-19) carries a skeleton hydrazonyl group in the carboxylate ligand.

#### Example 6

The photoconductor of Example 6 was prepared in the same way as that of Example 1 except that the metal atom of the zinc carboxylate represented by Formula (I-1) was replaced by tin.

#### Example 7

The photoconductor of Example 7 was prepared in the same way as that of Example 1 except that the metal atom of the zinc carboxylate represented by Formula (I-1) was replaced by cobalt.

#### Example 8

The photoconductor of Example 8 was prepared in the same way as that of Example 1 except that the metal atom of the zinc carboxylate represented by Formula (I-1) was replaced by nickel.

#### Example 9

The photoconductor of Example 9 was prepared in the same way as that of Example 1 except that the metal atom of the zinc carboxylate represented by Formula (I-1) was replaced by iron.

#### Example 10

The photoconductor of Example 10 was prepared in the same way as that of Example 1 except that the metal atom of the zinc carboxylate represented by Formula (I-1) was replaced by chromium.

#### Example 11

The photoconductor of Example 11 was prepared in the same way as that of Example 1 except that the charge transporting diamine compound represented by the following Formula (C) was used in place of the stilbene compound represented by Formula (B).

#### Example 12

The photoconductor of Example 12 was prepared in the same way as that of Example 11 except that the zinc carboxylate of Formula (II-1), carrying a skeleton stilbenyl group in the carboxylate ligand, was used instead of that represented by Formula (I-1).

#### Example 13

The photoconductor of Example 13 was prepared in the same way as that of Example 11 except that the zinc carboxylate represented by Formula (III-1), carrying a skeleton hydrazonyl group in the carboxylate ligand, was used instead of that represented by Formula (I-1).

#### Example 14

The photoconductor of Example 14 was prepared in the same way as that of Example 11 except that the zinc carboxylate represented by Formula (III-10), carrying a skeleton hydrazonyl group in the carboxylate ligand, was used instead of that represented by Formula (I-1).

#### Example 15

The photoconductor of Example 15 was prepared in the same way as that of Example 11 except that the zinc carboxylate represented by Formula (III-19), carrying a skeleton hydrazone group in the carboxylate ligand, was used in place of that represented by Formula (I-1).

#### Example 16

The photoconductor of Example 16 was prepared in the same way as that of Example 11 except that the metal atom in the zinc carboxylate represented by Formula (I-1) was replaced by a tin atom.

#### Example 17

The photoconductor of Example 17 was prepared in the same way as that of Example 11 except that the metal atom in the zinc carboxylate represented by Formula (I-1) was replaced by a cobalt atom.

#### Example 18

The photoconductor of Example 18 was prepared in the same way as that of Example 11 except that the metal atom in the zinc carboxylate represented by Formula (I-1) was replaced by a nickel atom.

#### Example 19

The photoconductor of Example 19 was prepared in the same way as that of Example 11 except that the metal atom in the zinc carboxylate represented by Formula (I-1) was replaced by an iron atom.

#### Example 20

The photoconductor of Example 20 was prepared in the same way as that of Example 11 except that the metal atom in the zinc carboxylate represented by Formula (I-1) was replaced by a chromium atom.

#### Comparative Example 1

The photoconductor of Comparative Example 1 was prepared in the same way as that in Example 1 except that the metal carboxylate was not incorporated into the charge transport layer.

#### Comparative Example 2

The photoconductor of Comparative Example 2 was prepared in the same way as that in Example 11 except that the metal carboxylate was not incorporated into the charge transport layer.

#### Evaluation of the Photoconductor

The following describes the evaluation of electric characteristics of the photoconductor of examples 1 to 20, and comparative examples 1 to 2.

The photoconductor was rotated and electrically charged to a potential of -650 V in darkness. The surface potential of the photoconductor, five seconds after halting rotation and charging, was measured. This measurement gives the retention rate of charged potential after five seconds, R5. Then, the surface of the photoconductor was subjected to continuous exposure to light. The potential-halving exposure  $E_{1/2}$ , which is the amount of exposure light energy required to attenuate potential from -600 V to -300 V, was measured.

Residual potential  $V_r$ , which is surface potential of the photoconductor exposed to a total amount of light energy of 5  $\mu\text{J}/\text{cm}^2$ , was measured.

In addition, the photoconductor was installed into a laser beam printer remodeled to measure surface potential of the photoconductor. Charged potential,  $V_i$ , and residual potential,  $V_r$ , at the initial and after 30,000 sheets of printing were measured.

#### TABLE 1

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Initial Electric Potential in Actual Machine  
 Characteristics Initial Use  
 After 30,000 printouts  
 Sample  
 R5 (%)  
 E1/2 (.mu.J/cm2)  
 Vr (-V)  
 Vi (-V)  
 Vr (-V)  
 Vi (-V)  
 Vr (-V)

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Ex. 1 96 0.09 32 680 52 668 80  
 Ex. 2 95 0.09 33 683 50 660 78  
 Ex. 3 96 0.09 31 685 55 667 90  
 Ex. 4 94 0.10 30 681 53 668 95  
 Ex. 5 95 0.10 31 680 52 670 92  
 Ex. 6 96 0.09 33 685 51 670 90  
 Ex. 7 94 0.10 32 680 50 669 95  
 Ex. 8 95 0.10 35 682 53 667 96  
 Ex. 9 95 0.11 32 683 57 668 90  
 Ex. 10 96 0.10 33 681 55 670 90  
 Ex. 11 96 0.11 53 685 73 670 95  
 Ex. 12 94 0.10 55 680 74 669 93  
 Ex. 13 95 0.12 57 682 75 667 107  
 Ex. 14 95 0.11 56 683 73 668 110  
 Ex. 15 95 0.10 55 681 76 670 105  
 Ex. 16 96 0.09 54 685 78 670 102  
 Ex. 17 94 0.10 53 680 76 669 110  
 Ex. 18 95 0.12 56 682 77 667 107  
 Ex. 19 95 0.10 55 683 75 668 110  
 Ex. 20 95 0.10 54 681 77 670 105  
 Comp. Ex. 1 94 0.10 35 682 55 640 260  
 Comp. Ex. 2 94 0.09 33 683 50 644 266

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Table 1 indicates that the photoconductor of Examples 1 to 20, which has the metal carboxylate represented by general formulae (I) to (III) incorporated into the charge transport layer, has variation in the charged potential and the residual potential suppressed on repetitive use of the photoconductor. This is compared with the photoconductor of Comparative Examples 1 and 2, which contain no metal carboxylate in the charge transport layer. In Comparative Examples 1 and 2, a large variation in the charged potential and the residual potential is demonstrated.

Incorporating a metal carboxylate into the charge transport layer of the photoconductor shows an excellent effect not only in the photoconductor for a laser beam printer incorporating phthalocyanine compound, but also in the photoconductor for a analog copier, a digital copier, and a facsimile machine.

Having described preferred embodiments of the invention with reference to the accompanying drawings, it is to be understood that the invention is not limited to those precise embodiments, and that various changes and modifications may be effected therein by one skilled in the art without departing from the scope or spirit of the invention as defined in the appended claims.

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## Claims

What is claimed is:



1. A photoconductor for electrophotography comprising:  
a conductive substrate;  
an under-coating layer on said conductive substrate;  
a photoconductive layer on said under-coating layer;  
said photoconductive layer having a charge generation layer and a charge transport layer; and  
said charge transport layer having a metal carboxylate represented by the following general Formula (I),  
wherein Ar<sub>1</sub> represents an optionally substituted arylene group, X represents a metal atom selected from the group consisting of tin, zinc, cobalt, nickel, iron, and chromium, and n represents the valence of X.
2. A photoconductor for electrophotography according to claim 1, wherein:  
said charge generation layer is on said under-coating layer; and  
said charge transport layer is on said charge generation layer.
3. A photoconductor for electrophotography according to claim 1, wherein Ar<sub>1</sub> represents an optionally substituted phenyl group.
4. A photoconductor for electrophotography according to claim 1, wherein Ar<sub>1</sub> represents an optionally substituted naphthyl group.
5. A photoconductor for electrophotography according to claim 1, wherein said optionally substituted arylene group is substituted with at least one of a halogen, a hydroxy group, a cyano group, a methyl group, and a methoxy group.
6. A photoconductor for electrophotography comprising:  
a conductive substrate;  
an under-coating layer on said conductive substrate;  
a photoconductive layer on said under-coating layer;  
said photoconductive layer having a charge generation layer and a charge transport layer; and  
said charge transport layer having a metal carboxylate represented by the following general Formula (II),  
wherein Ar<sub>1</sub> represents an optionally substituted arylene group, X represents a metal atom selected from the group consisting of tin, zinc, cobalt, nickel, iron, and chromium, and n represents the valence of X.
7. A photoconductor for electrophotography according to claim 6, wherein:  
said charge generation layer is on said under-coating layer; and  
said charge transport layer is on said charge generation layer.
8. A photoconductor for electrophotography according to claim 6, wherein Ar<sub>1</sub> represents an optionally substituted phenyl group.
9. A photoconductor for electrophotography according to claim 6, wherein Ar<sub>1</sub> represents an optionally substituted naphthyl group.
10. A photoconductor for electrophotography according to claim 6, wherein said optionally substituted arylene group is substituted with at least one of a halogen, a hydroxy group, a cyano group, a methyl group, and a methoxy group.
11. A photoconductor for electrophotography comprising:  
a conductive substrate;  
an under-coating layer on said conductive substrate;  
a photoconductive layer on said under-coating layer;  
said photoconductive layer having a charge generation layer and a charge transport layer; and  
said charge transport layer having a metal carboxylate represented by the following general Formula (III),  
wherein Ar<sub>1</sub> represents an optionally substituted arylene group, Ar<sub>1</sub> represents one of the group consisting of an alkyl group, an optionally substituted aryl group, an arylalkyl group, and a hydrogen atom, X represents a metal atom selected from the group consisting of tin, zinc, cobalt, nickel, iron, and chromium, and n represents the valence of X.
12. A photoconductor for electrophotography according to claim 11, wherein:  
said charge generation layer is on said under-coating layer; and  
said charge transport layer is on said charge generation layer.

13. A photoconductor for electrophotography according to claim 11, wherein Ar1 represents an optionally substituted phenyl group.

14. A photoconductor for electrophotography according to claim 11, wherein Ar1 represents an optionally substituted naphthyl group.

15. A photoconductor for electrophotography according to claim 11, wherein said optionally substituted arylene group is substituted with at least one of a halogen, a hydroxy group, a cyano group, a methyl group, and a methoxy group.

16. A photoconductor for electrophotography according to claim 11, wherein Ar1 is an optionally substituted phenyl group.

17. A photoconductor for electrophotography according to claim 16, wherein said optionally substituted phenyl group is substituted with at least one of a methyl group and a hydroxy group.

18. A photoconductor for electrophotography according to claim 11, wherein Ar2 is a methyl group.

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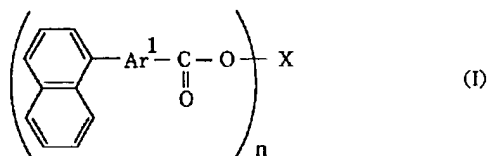
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(54) 【発明の名称】 電子写真用感光体

(57) 【要約】

【課題】 初期と繰り返し使用後との間の帯電電位および残留電位の変動差が小さく、良好な画像を得ることができる有機電子写真用感光体を提供する。

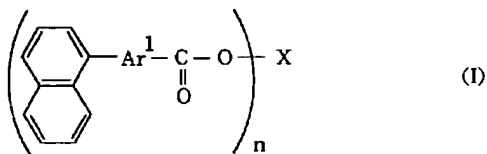
【解決手段】 導電性基体上に、有機化合物を主成分とした下引き層と、電荷発生層および電荷輸送層を順次積層してなる感光層とを備えた機能分離積層型電子写真用感光体において、前記電荷輸送層が下記一般式 (I)、



(式中、Ar<sup>1</sup> は、置換基を有してもよい芳香族残基、Xは錫、亜鉛、コバルト、ニッケル、鉄またはクロム、nはXの原子価) で表される金属塩を含有する。

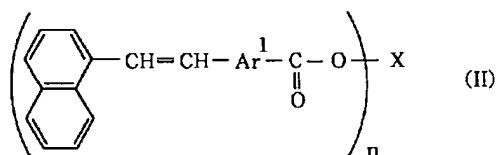
## 【特許請求の範囲】

【請求項1】 導電性基体上に、有機化合物を主成分とした下引き層と、電荷発生層および電荷輸送層を順次積層してなる感光層とを備えた機能分離積層型電子写真用感光体において、前記電荷輸送層が下記一般式（I）、



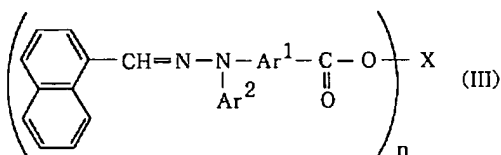
（式中、 $\text{Ar}^1$  は、置換基を有してもよい芳香族残基を表し、Xは錫、亜鉛、コバルト、ニッケル、鉄およびクロムからなる群から選ばれる金属原子を表し、nはXの原子価を表す。）で表される金属塩を含有することを特徴とする電子写真用感光体。

【請求項2】 請求項1記載の電子写真用感光体において、前記一般式（I）で表される金属塩に代え、前記電荷輸送層が下記一般式（II）、



（式中、 $\text{Ar}^1$ 、nおよびXは前記のものと同じものを表す。）で表される、配位子中にスチルベン骨格を有する金属塩を含有することを特徴とする電子写真用感光体。

【請求項3】 請求項1記載の電子写真用感光体において、前記一般式（I）で表される金属塩に代え、前記電荷輸送層が下記一般式（III）、



（式中、 $\text{Ar}^1$ 、nおよびXは前記のものと同じものを表し、 $\text{Ar}^2$  はアルキル基、置換基を有してもよいアリール基、アラルキル基、または水素原子を表す。）で表される、配位子中にヒドラゾン骨格を有する金属塩を含有することを特徴とする電子写真用感光体。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、電子写真方式のプリンタおよび複写機等に用いられる電子写真用感光体に関し、詳しくは有機材料を主成分としてなる電荷輸送層の構成材料の改良技術に関する。

## 【0002】

【従来の技術】 電子写真用感光体（以下単に「感光体」と称する場合あり）は、導電性基体上に光導電機能を有する感光層を積層した構造を基本構造とする。近年、電荷の発生や輸送を担う機能成分として有機化合物を感光層に用いる有機電子写真用感光体の研究開発が、材料の多様性、高生産性、安全性などの利点から活発に行われ、複写機やプリンタなどへの適用が進められている。

【0003】 感光体には、暗所で表面電荷を保持する機能、光を受容して電荷を発生する機能、さらには発生した電荷を輸送する機能が必要であり、これらの機能を併せ持った単層の感光層を備えた、いわゆる単層型感光体と、主として光受容時に電荷発生の機能を担う電荷発生層と、暗所で表面電荷を保持する機能および光受容時に電荷発生層にて発生した電荷を輸送する機能を担う電荷輸送層とに機能分離した層を積層した感光層を備えた、いわゆる機能分離積層型感光体がある。

【0004】 最近では、有機顔料を電荷発生材料として、これを樹脂バインダーとともに有機溶媒中に溶解、分散させた塗布液を塗布成膜した層を電荷発生層とし、また有機低分子化合物を電荷輸送材料として、これを樹脂バインダーとともに有機溶媒中に溶解、分散させた塗布液を塗布成膜した層を電荷輸送層とし、これらの層を積層して感光層とする機能分離積層型電子写真用感光体が主流となってきている。

## 【0005】

【発明が解決しようとする課題】 しかしながら、現在有機感光体は、感光体に求められる要求特性を必ずしも十分に満足しているとはいえず、特に繰り返し使用時における電気特性の安定性は、その向上が強く望まれている要求特性の一つである。具体的には、感光体が実機で連続して繰り返し使用されたときに、帯電電位または残留電位の変動が生じ、印字品質の低下を招くという問題がある。

【0006】 上記のような電位変動の要因としては、感光体の露光、除電などのプロセスにおいて発生する有機膜中への電荷の蓄積や、実機内での連続使用に伴う光、熱およびオゾン並びに使用環境の温湿度条件の変化などによる有機材料の疲労、劣化といったことが挙げられる。特に、電荷の蓄積については、電荷発生層および電荷輸送層中、またはその界面における電荷のトラップに起因するものと考えられており、電荷発生材料、電荷輸送材料を中心に改良が進められているが、まだこの問題を十分に解決し得る手段、材料は見出されていない。

【0007】 また、上述した繰り返し使用時における帯電電位および残留電位の変動を抑制する目的で、電荷輸送層に添加剤を添加しても、従来公知の特定の添加剤では十分な効果は得られておらず、添加剤によっては帯電性の低下または残留電位の上昇を引き起こし、却ってマイナスイメージ効果となることもある。

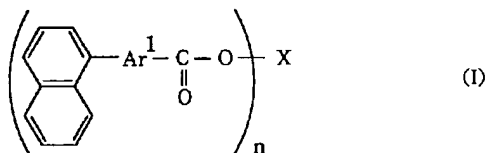
【0008】 そこで本発明の目的は、初期と繰り返し使

用後との間の帯電電位および残留電位の変動差が小さく、良好な画像を得ることができる有機電子写真用感光体を提供することにある。

【0009】

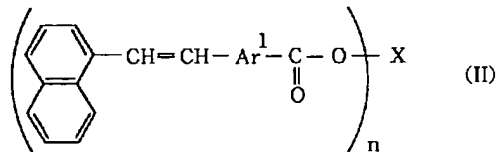
【課題を解決するための手段】本発明者らは、いかなる電荷発生層および電荷輸送層と共に用いても、繰り返し使用時の帯電電位および残留電位の変動抑制に十分な効果があり、しかも他の電気性能に影響を与えることのない添加剤について鋭意検討した結果、電荷輸送層への特定金属塩の添加により非常に優れた効果が得られることを見出し、本発明を完成するに至った。

【0010】即ち、本発明の電子写真用感光体は、導電性基体上に、有機化合物を主成分とした下引き層と、電荷発生層および電荷輸送層を順次積層してなる感光層とを備えた機能分離積層型電子写真用感光体において、前記電荷輸送層が下記一般式(I)、



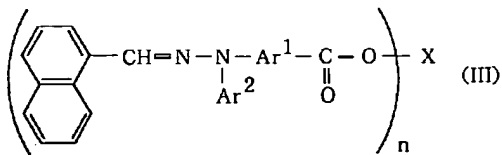
(式中、 $\text{Ar}^1$ は、置換基を有してもよい芳香族残基を表し、Xは錫、亜鉛、コバルト、ニッケル、鉄およびクロムからなる群から選ばれる金属原子を表し、nはXの原子価を表す。)で表される金属塩を含有することを特徴とするものである。

【0011】また、本発明の電子写真用感光体は、前記電子写真用感光体において、前記一般式(I)で表される金属塩に代え、前記電荷輸送層が下記一般式(II)、



(式中、 $\text{Ar}^1$ 、nおよびXは前記のものと同じものを表す。)で表される、配位子中にスチルベン骨格を有する金属塩を含有することを特徴とするものである。

【0012】さらに、本発明の電子写真用感光体は、前記電子写真用感光体において、前記一般式(I)で表される金属塩に代え、前記電荷輸送層が下記一般式(III)、



(式中、 $\text{Ar}^1$ 、nおよびXは前記のものと同じものを

表し、 $\text{Ar}^2$ はアルキル基、置換基を有してもよいアリール基、アラルキル基、または水素原子を表す。)で表される、配位子中にヒドラゾン骨格を有する金属塩を含有することを特徴とするものである。

【0013】

【発明の実施の形態】以下、本発明の実施の形態を具体的に説明する。図1は、本発明の感光体の一構成例を示す模式的断面図であり、導電性基体1の上に、下引き層2を介して、電荷発生層4と電荷輸送層5とが順次積層されてなる感光層3が設けられた構成の負帯電型の機能分離積層型感光体である。

【0014】導電性基体1は、感光体の一電極としての役目と同時に感光体を構成する各層の支持体ともなっており、円筒状、板状、フィルム状などいずれの形状でもよく、材質的には、アルミニウム、ステンレス鋼、ニッケルなどの金属類、あるいはガラス、樹脂などの表面に導電処理を施したものでもよい。

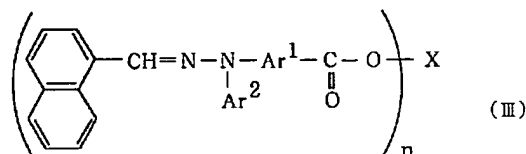
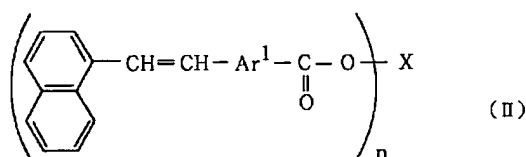
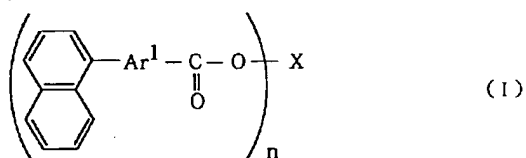
【0015】下引き層2は、樹脂を主成分とする層やアルマイトなどの金属酸化皮膜からなり、導電性基体から感光層への電荷の注入性を制御するため、または基体表面の欠陥の被覆、感光層と下地との接着性の向上などの目的で必要に応じて設けられる。下引き層に用いられる樹脂材料としては、カゼイン、ポリビニルアルコール、ポリアミド、メラミン、セルロースなどの絶縁性高分子、ポリチオフェン、ポリピロール、ポリアニリンなどの導電性高分子が挙げられ、これらの樹脂は単独で、あるいは適宜組み合わせで混合して用いることができる。また、これらの樹脂に二酸化チタン、酸化亜鉛などの金属酸化物を含有することができる。

【0016】電荷発生層4は、電荷発生材料として有機光導電性材料を真空蒸着または有機光導電性材料の粒子を樹脂バインダー中に分散させた溶液を塗布することにより形成され、光を受容して電荷を発生する。電荷発生効率が高いことと同時に発生した電荷の電荷輸送層5への注入性が重要であり、電場依存性が少なく低電場でも注入の良いことが望ましい。電荷発生材料としては、無金属フタロシアニン、チタニルフタロシアニン等の各種フタロシアニン化合物、ビスアゾ化合物等の各種アゾ化合物の他、キノン、インジゴ、シアニン、スクアリリウム、アズレニウム、ピリリウム化合物等の顔料や染料等を用いることができる。樹脂バインダーとしては、ポリエステル樹脂、ポリビニルアセテート、ポリアクリル酸エステル、ポリメタクリル酸エステル等のポリエステル、ポリカーボネート、ポリビニルアセトアセタール、ポリビニルプロピオナール、ポリビニルブチラール、フェノキシ樹脂、エポキシ樹脂、ウレタン樹脂、セルロースエステル、セルロースエーテルなどを適宜組み合わせで使用することが可能である。

【0017】樹脂バインダーと電荷発生材料との比率は、樹脂バインダー10重量部に対し電荷発生材料は5

から500重量部、好ましくは10から100重量部である。さらに電荷発生層4は、その上部に電荷輸送層5が積層されるので、その膜厚は電荷発生物質の光吸収係数によって決まり、一般的には5 $\mu$ m以下であり、好適には1 $\mu$ m以下である。

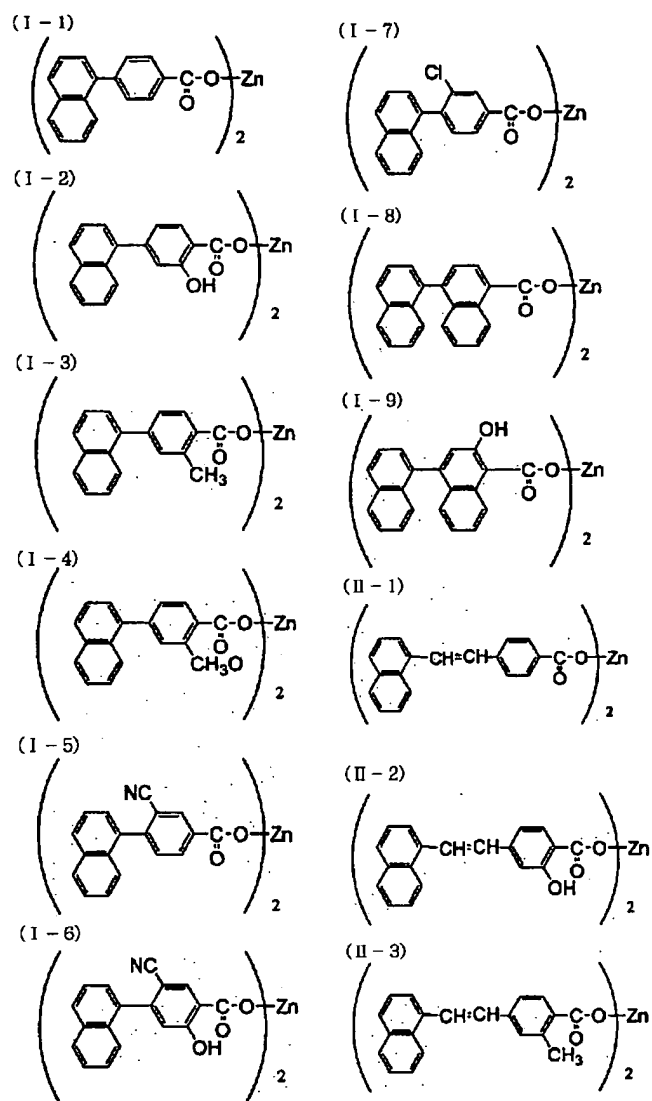
【0018】電荷輸送層5は、電荷輸送材料、樹脂バインダーおよび、下記一般式(I)～(III)のうちのいずれかで表される金属塩により構成される。

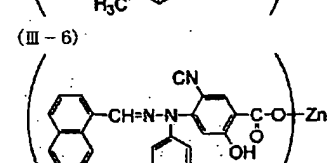
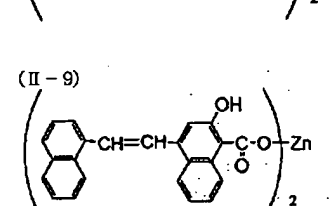
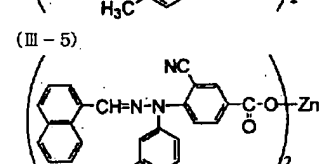
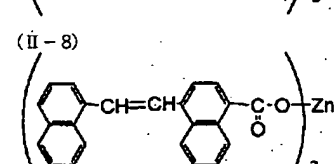
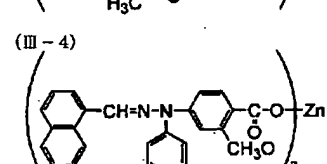
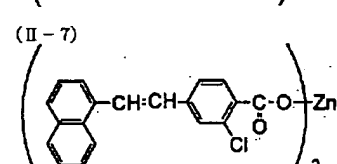
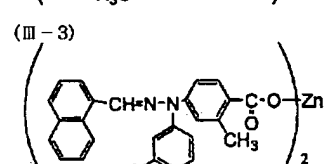
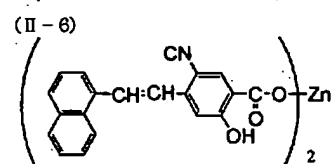
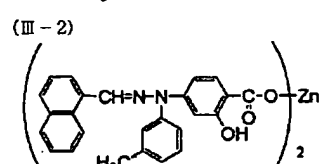
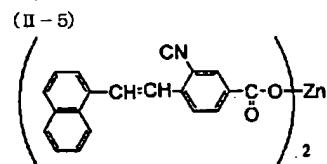
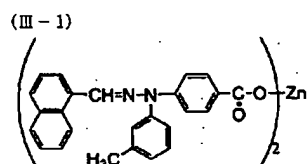
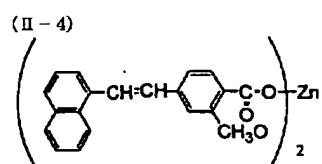


【0019】前記式(I)～(III)中、 $\text{Ar}^1$ は、置換基を有してもよい芳香族残基を表し、Xは錫、亜鉛、コバルト、ニッケル、鉄およびクロムからなる群から選ばれる金属原子を表し、nはXの原子価を表し、 $\text{Ar}^2$ はアルキル基、置換基を有してもよいアリール基、アラルキル基、または水素原子を表す。好ましくは、 $\text{Ar}^1$ はアルキル基、アリール基、水酸基、アルコキシ基、アリールオキシ基、アルキルカルボニル基、アリールカルボニル基、アルコキシカルボニル基、アリールオキシカルボニル基、カルボキシル基、シアノ基などの置換基を有してもよいベンゼン、ナフタレンまたはアントラセンなどの芳香環残基を表す。

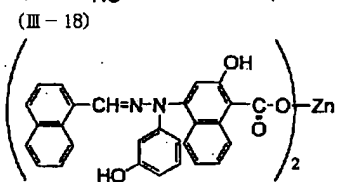
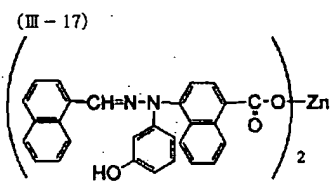
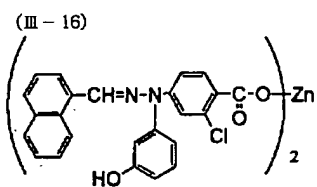
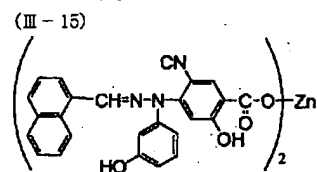
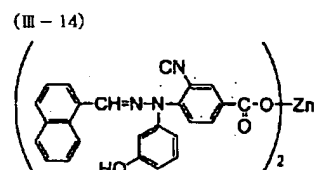
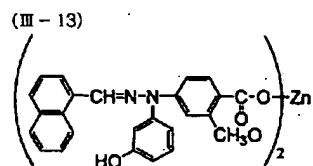
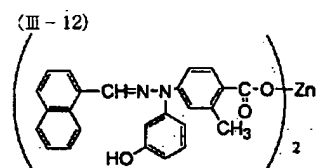
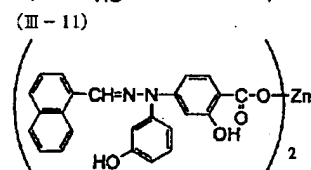
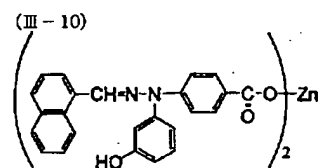
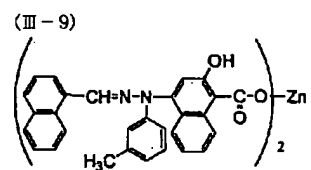
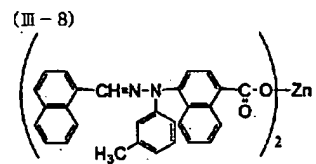
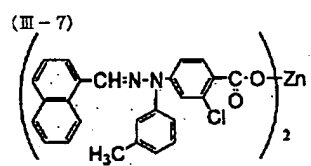
【0020】次に、一般式(I)～(III)で表される金属原子中のXが亜鉛である金属塩の主な具体例を示すが、これらに限定されるものではなく、金属原子が錫、コバルト、ニッケル、鉄またはクロムでもよい。なお、例示金属塩(I-1)から(I-9)までは上記一般式(I)に関するもの、例示金属塩(II-1)から(II-9)までは上記一般式(II)に関するもの、例示金属塩(III-1)から(III-27)までは上記一般式(III)に関するものである。

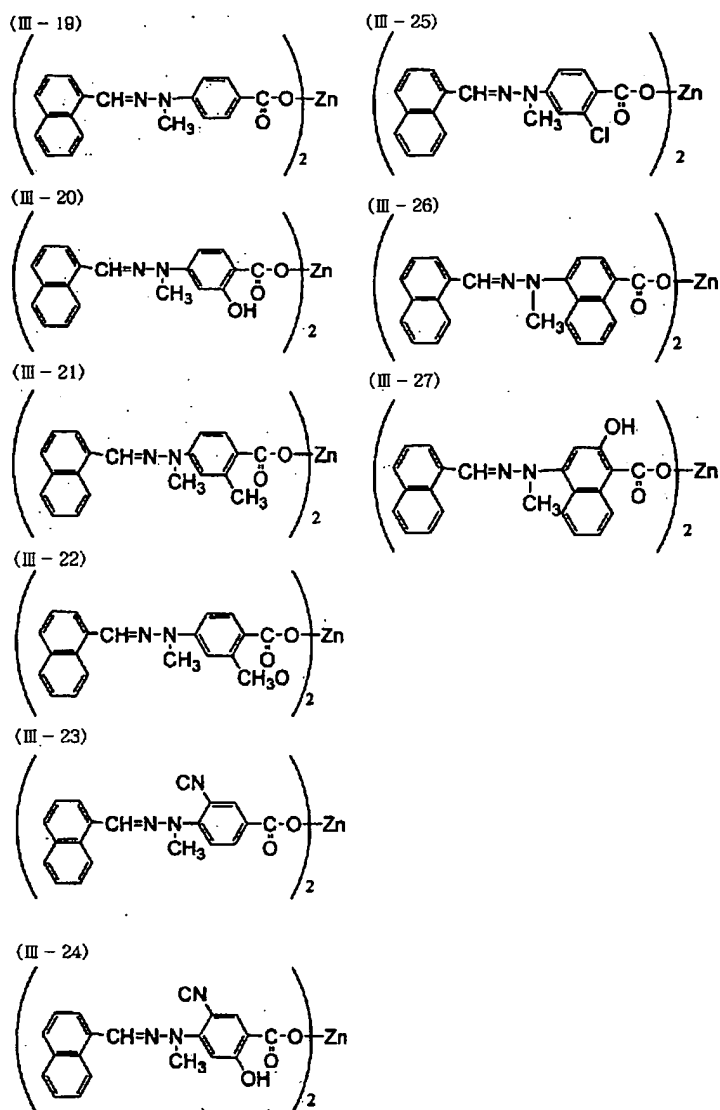
【0021】











【0025】電荷輸送材料としては、ヒドラゾン化合物、ブタジエン化合物、ジアミン化合物、インドール化合物、インドリン化合物、スチルベン化合物、ジスチルベン化合物などが夫々単独で、あるいは適宜組み合わせで混合して用いられる。樹脂バインダーとしては、ビスフェノールA型、ビスフェノールZ型、ビスフェノールA型-ビフェニル共重合体などのポリカーボネート樹脂、ポリスチレン樹脂、ポリフェニレン樹脂などが夫々単独で、あるいは適宜組み合わせで混合して用いられる。

【0026】電荷輸送材化合物の使用量は、樹脂バインダー100重量部に対し2～50重量部、好適には3～30重量部である。電荷輸送層の膜厚としては、実用上有効な表面電位を維持するためには3～50 $\mu$ mの範囲が好ましく、より好適には15～40 $\mu$ mである。

【0027】また、上述した本発明に係る金属塩を電荷

輸送層に添加する割合は、通常、バインダー樹脂100重量部に対して0.01～10重量部、好適には0.1～3重量部である。

【0028】さらに、下引き層、電荷輸送層には感度の向上、残留電位の減少、あるいは耐環境性や有害な光に対する安定性の向上などを目的として、必要に応じて電子受容性物質、酸化防止剤、光安定剤などを添加することができる。このような目的で用いられる化合物としては、トコフェロールなどのクロマール誘導体、エーテル化合物、エステル化合物、ポリアリールアルカン化合物、ハイドロキノン誘導体、ジエーテル化合物、ベンゾフェノン誘導体、ベンゾトリアゾール誘導体、チオエーテル化合物、フェニレンジアミン誘導体、ホスホン酸エステル、亜リン酸エステル、フェノール化合物、ヒンダードフェノール化合物、直鎖アミン化合物、環状アミン化合物、ヒンダードアミン化合物などが挙げられ

るが、これらに限定されるものではない。

【0029】さらに、感光層中には、形成した膜のレベリング性の向上や、さらなる潤滑性の付与を目的として、シリコンオイルやフッ素系オイルなどのレベリング剤を含有させることもできる。

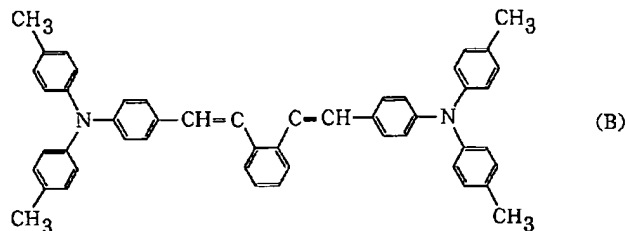
【0030】さらにまた、感光層表面に耐環境性や機械的強度をより向上させる目的で、必要に応じて表面保護層を設けてもよい。表面保護層は、機械的ストレスに対する耐久性および耐環境性に優れた材料で構成され、電荷発生層が感応する光をできるだけ低損失で透過させる性能を有していることが望まれる。

【0031】

【実施例】以下、本発明を実施例について説明する。

#### 実施例1

導電性基体としてアルミニウム円筒を用い、その外周面に下引き層としてアルコール可溶性ナイロン（東レ（株）製「CM 8000」）5重量部と、アミノシラン処理された酸化チタン微粒子5重量部とをメタノール90重量部に溶解、分散させて調製した塗布液を浸積塗工し、温度100℃で30分間乾燥して、膜厚約3μm



で表されるスチルベン化合物90重量部と、樹脂バインダーとしてポリカーボネート樹脂（出光興産（株）製「タフゼットB-500」）110重量部と、前記例示構造式（I-1）の亜鉛塩0.1重量部とを、ジクロロメタン925重量部に溶解した塗布液を塗布成膜し、温度90℃で60分間乾燥して、膜厚約35μmの電荷輸送層を形成し、有機電子写真用感光体を作製した。

#### 【0034】実施例2

実施例1の亜鉛塩を配位子中にスチルベン骨格を有する前記例示構造式（II-1）の亜鉛塩に代えた以外は、実施例1と同様の方法で有機電子写真用感光体を作製した。

#### 【0035】実施例3

実施例1の亜鉛塩を配位子中にヒドラゾン骨格を有する前記例示構造式（III-1）の亜鉛塩に代えた以外は、実施例1と同様の方法で有機電子写真用感光体を作製した。

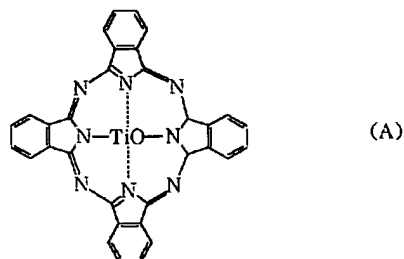
#### 【0036】実施例4

実施例1の亜鉛塩を配位子中にヒドラゾン骨格を有する前記例示構造式（III-10）の亜鉛塩に代えた以外は、実施例1と同様の方法で有機電子写真用感光体を作製した。

#### 【0037】実施例5

の下引き層を形成した。

【0032】この下引き層上に、電荷発生材料として下記構造式（A）、



で表されるオキシチタニウムが配位したフタロシアニン1重量部と、樹脂バインダーとしてポリビニルピチラール樹脂（積水化学（株）製「エスレックKS-1」）

1.5重量部とをジクロロメタン60重量部に溶解、分散させて調製した塗布液を浸積塗工し、温度80℃で30分間乾燥して、膜厚約0.3μmの電荷発生層を形成した。

【0033】この電荷発生層上に、電荷輸送材料として下記構造式（B）、

実施例1の亜鉛塩を配位子中にヒドラゾン骨格を有する前記例示構造式（III-19）の亜鉛塩に代えた以外は、実施例1と同様の方法で有機電子写真用感光体を作製した。

#### 【0038】実施例6

実施例1で使用了した亜鉛塩の金属原子を錫原子に代えた以外は、実施例1と同様の方法で有機電子写真用感光体を作製した。

#### 【0039】実施例7

実施例1で使用了した亜鉛塩の金属原子をコバルト原子に代えた以外は、実施例1と同様の方法で有機電子写真用感光体を作製した。

#### 【0040】実施例8

実施例1で使用了した亜鉛塩の金属原子をニッケル原子に代えた以外は、実施例1と同様の方法で有機電子写真用感光体を作製した。

#### 【0041】実施例9

実施例1で使用了した亜鉛塩の金属原子を鉄原子に代えた以外は、実施例1と同様の方法で有機電子写真用感光体を作製した。

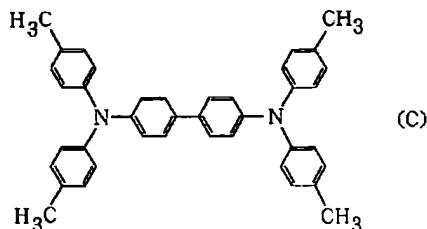
#### 【0042】実施例10

実施例1で使用了した亜鉛塩の金属原子をクロム原子に代えた以外は、実施例1と同様の方法で有機電子写真用感光体を作製した。

光体を作製した。

【0043】実施例11

実施例1で使用した電荷輸送材料を、下記構造式(C)、



で表されるジアミン化合物に代えた以外は、実施例1と同様の方法で有機電子写真用感光体を作製した。

【0044】実施例12

実施例11で使用した亜鉛塩を配位子中にスチルベン骨格を有する前記例示構造式(II-1)の亜鉛塩に代えた以外は、実施例11と同様の方法で有機電子写真用感光体を作製した。

【0045】実施例13

実施例11で使用した亜鉛塩を配位子中にヒドラゾン骨格を有する前記例示化合物(III-1)の亜鉛塩に代えた以外は、実施例11と同様の方法で有機電子写真用感光体を作製した。

【0046】実施例14

実施例11で使用した亜鉛塩を配位子中にヒドラゾン骨格を有する前記例示化合物(III-10)の亜鉛塩に代えた以外は、実施例11と同様の方法で有機電子写真用感光体を作製した。

【0047】実施例15

実施例11で使用した亜鉛塩を配位子中にヒドラゾン骨格を有する前記例示化合物(III-19)の亜鉛塩に代えた以外は、実施例11と同様の方法で有機電子写真用感光体を作製した。

【0048】実施例16

実施例11で使用した亜鉛塩の金属原子を錫原子に代えた以外は、実施例11と同様の方法で有機電子写真用感光体を作製した。

【0049】実施例17

実施例11で使用した亜鉛塩の金属原子をコバルト原子に代えた以外は、実施例11と同様の方法で有機電子写

真用感光体を作製した。

【0050】実施例18

実施例11で使用した亜鉛塩の金属原子をニッケル原子に代えた以外は、実施例11と同様の方法で有機電子写真用感光体を作製した。

【0051】実施例19

実施例11で使用した亜鉛塩の金属原子を鉄原子に代えた以外は、実施例11と同様の方法で有機電子写真用感光体を作製した。

【0052】実施例20

実施例11で使用した亜鉛塩の金属原子をクロム原子に代えた以外は、実施例11と同様の方法で有機電子写真用感光体を作製した。

【0053】比較例1

前記実施例において使用した金属塩を電荷輸送層中に添加せずに、実施例1と同様の方法で有機電子写真用感光体を作製した。

【0054】比較例2

前記実施例において使用した金属塩を電荷輸送層中に添加せずに、実施例11と同様の方法で有機電子写真用感光体を作製した。

【0055】感光体の評価

上記実施例1～20および比較例1、2の感光体の電気特性を、下記の方法で評価した。作製した感光体を暗所で-650Vに帯電せしめた後、回転を停止させた感光体ドラムの表面電位の5秒後の表面電位の保持率を求めた。続いて、感光体ドラム表面に露光光を照射し続け、帯電電位が-600Vから-300Vに到達するのに必要な露光量を半減露光量 $E_{1/2}$ と呼び、半減露光量を求めた。また、上記感度測定においてトータル光量 $5\mu\text{J}/\text{cm}^2$ の露光光を照射した直後の感光体表面電位を残留電位と呼び、残留電位を求めた。

【0056】また、作製した感光体を、感光体の表面電位を測定すべく改造を施したレーザービームプリンターに搭載し、初期および3万枚印字後の帯電電位および残留電位変動の抑制効果を評価した。その結果を表1に示す。

【0057】

【表1】

| 試料    | 初期電気特性            |  |              | 実機内電位        |              |              |              |
|-------|-------------------|--|--------------|--------------|--------------|--------------|--------------|
|       |                   |  |              | 初期           |              | 3万枚後         |              |
|       | 5秒後<br>保持率<br>(%) | 半減露光量<br>( $\mu\text{J}/\text{cm}^2$ ) | 残留電位<br>(-V) | 帯電電位<br>(-V) | 残留電位<br>(-V) | 帯電電位<br>(-V) | 残留電位<br>(-V) |
| 実施例1  | 96                | 0.09                                   | 32           | 680          | 52           | 668          | 80           |
| 実施例2  | 95                | 0.09                                   | 33           | 683          | 50           | 660          | 78           |
| 実施例3  | 96                | 0.09                                   | 31           | 685          | 55           | 667          | 90           |
| 実施例4  | 94                | 0.10                                   | 30           | 681          | 53           | 668          | 95           |
| 実施例5  | 95                | 0.10                                   | 31           | 680          | 52           | 670          | 92           |
| 実施例6  | 96                | 0.09                                   | 33           | 685          | 51           | 670          | 90           |
| 実施例7  | 94                | 0.10                                   | 32           | 680          | 50           | 669          | 95           |
| 実施例8  | 95                | 0.10                                   | 35           | 682          | 53           | 667          | 96           |
| 実施例9  | 95                | 0.11                                   | 32           | 683          | 57           | 668          | 90           |
| 実施例10 | 96                | 0.10                                   | 33           | 681          | 55           | 670          | 90           |
| 実施例11 | 96                | 0.11                                   | 53           | 685          | 73           | 670          | 95           |
| 実施例12 | 94                | 0.10                                   | 55           | 680          | 74           | 669          | 93           |
| 実施例13 | 95                | 0.12                                   | 57           | 682          | 75           | 667          | 107          |
| 実施例14 | 95                | 0.11                                   | 56           | 683          | 73           | 668          | 110          |
| 実施例15 | 95                | 0.10                                   | 55           | 681          | 76           | 670          | 105          |
| 実施例16 | 96                | 0.09                                   | 54           | 685          | 78           | 670          | 102          |
| 実施例17 | 94                | 0.10                                   | 53           | 680          | 76           | 669          | 110          |
| 実施例18 | 95                | 0.12                                   | 56           | 682          | 77           | 667          | 107          |
| 実施例19 | 95                | 0.10                                   | 55           | 683          | 75           | 668          | 110          |
| 実施例20 | 95                | 0.10                                   | 54           | 681          | 77           | 670          | 105          |
| 比較例1  | 94                | 0.10                                   | 35           | 682          | 55           | 640          | 260          |
| 比較例2  | 94                | 0.09                                   | 33           | 683          | 50           | 644          | 266          |

【0058】上記表1の結果から明らかなように、電荷輸送層中に上述の一般式(I)～(III)で表される金属塩を用いた、本発明における実施例1～20の感光体は、電荷輸送層中に金属塩を含有しない比較例1および2の感光体と比較して、連続使用後の帯電電位および残留電位変動の抑制効果があることが判明した。

【0059】また、上記実施例に示したフタロシアニン化合物を用いるレーザービームプリンター用感光体のみならず、アナログ複写機用、デジタル複写機用、ファクシミリ用感光体においても、本発明に係る金属塩を電荷輸送層中に含有させることにより、実際のプリンター、デジタル複写機、ファクシミリに搭載した際に、同様な効果が得られた。

【0060】

【発明の効果】本発明により、初期と繰り返し使用後との間の帯電電位および残留電位の変動差が小さく、良好な画像を得ることができる有機電子写真用感光体を提供することが可能となる。

【図面の簡単な説明】

【図1】本発明に係る負帯電機能分離積層型電子写真用感光体の模式的断面図である。

【符号の説明】

- 1 導電性基体
- 2 下引き層
- 3 感光層
- 4 電荷発生層
- 5 電荷輸送層

【図1】

